Kreiling

An Improved Victor Meyer Vapor Density Apparatus.

AN IMPROVED VICTOR MEYER VAPOR DENSITY APPARATUS

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Robert Graham Kreiling

ENTITLED An Improved Victor Meyer Vapor Density Apparatus.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering.

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TABLE OF CONTENTS

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I. THEORETICAL

All vapor density methods for the determination of molecular weights are based upon the gas law as expressed in the equation $pv = RT$. The numerical value of the constant R is usually calculated by allowing p to represent atmospheric pressure at sea level;T,0°C.;and V the volume occupied by a gram molecule of a gas under the above conditions of temperature and pressure.If more or less than a gram molecule of a gas or vapor be under consideration an additional factor n is introduced to avoid the necessity of changing the value of R.The general expression of the gas law then becomes $PV = nRT$. Since n is the number of molecules or the fractional part of a molecule employed its value may be represented by W/M in which W is the weight of substance used and M is its molecular weight. Substituting this value for n we have $PV = WRT/M$, or $M = WRT/PV$. In this equation R is constant but W,T,P,and V are variable quantities. It is evident that if in a determination,these factors are available,the molecular weight of the substance may be calculated.

In order to take into account the attractive forces between the molecules of gases as well as the volumes which the molecules themselves actually fill and thus to obtain an equation which would hold more accurately than the perfect

gas law, van der Waal's equation[a] must be used. van der Waal's equation of state for one mole of a gas is:-

$$\left(p + \frac{a}{V_0^2}\right)(V_0 - b) = RT$$

a and b being constants characteristic of the gas in question.

The characteristic constants a and b of this equation have been found to bear a definite relation to the critical constants of the gas, and with the aid of this empirical relation Berthelot modified the equation of van der Waals by substituting in place of a and b their values expressed in terms of the critical constonts of the gas. The resulting equation after an algebraic rearrangement may be expressed as follows:[a]-

$$M = \frac{DRT}{p}\left(1 + \left\{\frac{9T_c(T^2 - 6T_c^2)}{128\,p_c T^3}\right\}p\right)$$

where p , the critical pressure, is the pressure required to condense the gas at its critical temperature, T , the critical temperature, is the highest temperature at which the gas can be liquefied by increase of pressure, and the other quantities have the significance previously given to them.

Corrections were made for aqueous tension, taking into account the humidity of the air as directed by Evans[b].

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[a] Washburn, "Principles of Physical Chemistry".

[b] Jour. Amer. Chem. Soc., XXXV., p.958 (1913)

II. HISTORICAL

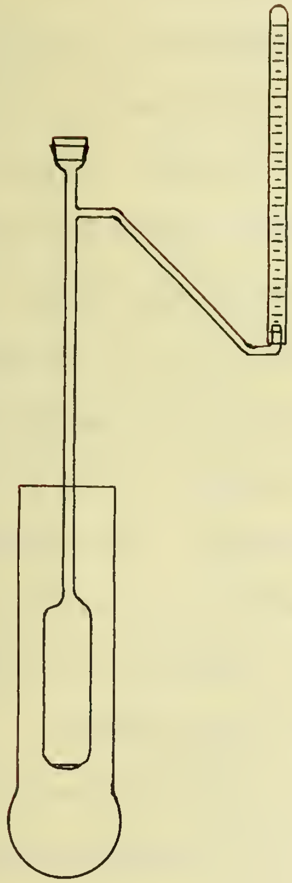

Figure I.

Victor Meyer, in 1866, constructed a piece of apparatus as shown in the accompanying drawing for the determination of the molecular weights of volatile liquids. The drawing and the following description are taken from Victor Meyer's original paper.

A glass tube of rather more than 100 c.c. capacity, closed at one end is drawn out to a tube at the other, about 1/7 the original diameter, terminating in an enlargement which admits an India rubber cork accurately adjusted to a mark on the tube. At a short distance below this mark an exit tube leaves the narrow portion at right angles, to pass, after being suitably bent, beneath the surface of mercury contained in a trough. Heat is applied to the lower portion of the apparatus by bringing it into the vapour of a liquid kept boiling in a second larger tube. When the air in the apparatus has reached a constant expansion at the temperature of the experiment, i.e., when no more bubbles escape

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Berichte, XI, p.1867

from the exit tube,a graduated jar filled with water is brought over the mouth of the latter,the cork removed,the weighed substance introduced,and the cork rapidly replaced.The substance is quickly vaporized and the vapour expels equivalent volume of air by the exit tube into the graduated jar.This is measured under ordinary conditions of pressure and temperature and from this quantity,after correction,the required vapour density is at once known. Fair results were obtained with this apparatus,and it was shown that the two sources of error to which it is subject,those due to diffusion and to discrepancy between the volumes of two mutual indifferent gases in contact with each other,and the sum of their volumes when isolated,are without sensible influence.

There have been several improvements made on this particular style of apparatus in the method of admitting the substance,the latest and most satisfactory being that designed by D.A.MacInnes from a suggestion of Dr.K.A.Clark. This is shown in figure III.

Various forms of apparatus using the same principles have been used by Philip Blackman,but most of them have been too elaborate in construction and manipulation,and results obtained have been no better than with the more simple apparatus previously described. Harry B.Weiser has designed a

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Jour.Phys.Chem. XII, p.66I, 666, 679

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piece of apparatus, the details of which are given in figure II. This apparatus is important in this connection as one of the pieces of apparatus used by the author is very similar in principle.

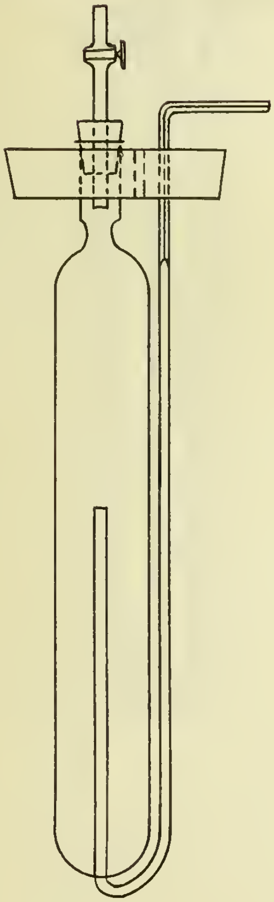


Figure II.

III. EXPERIMENTAL

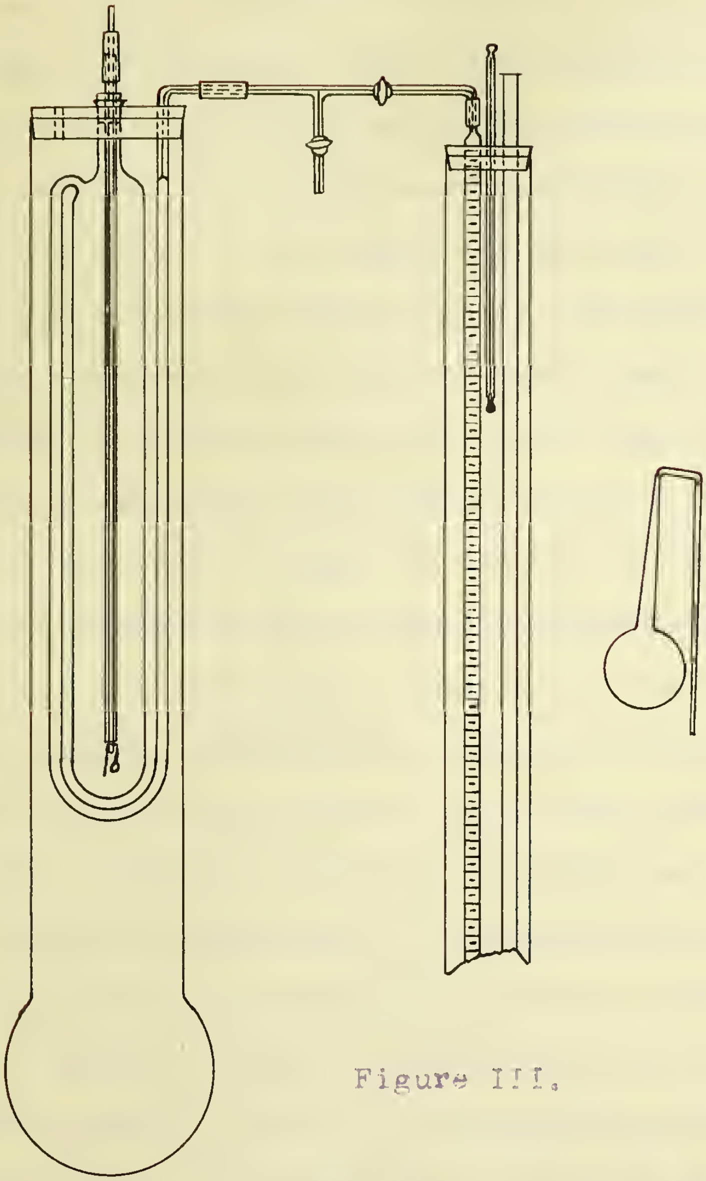


Figure III.

The vapourizing vessel shown in figure III is in principle the same as that used by H.B. Weiser. This was the first piece of apparatus used. The vapourizing vessel was 3 cm. in diameter and 20 cm. long, closed at one end, and tapering to a neck I.5 cm. in diameter and 4 cm. long. The tube which was bent around the vessel proper as shown, was 4 mm. in diameter and terminated in a capillary

tube I mm. in diameter. The substance used was contained in a bulb such as that shown in the accompanying drawing. The outer jacket was 7 cm. in diameter and 40 cm. long with a bulb at one end and the other end open. The substance whose vapour was to be used for heating was put in the bulb, the latter being abiut half filled. This was fitted with a three hole rubber stopper; one hole in the center for the neck of the vapourizing vessel, one for the capillary exit tube, and one for a steam outlet. The stopper was split. The capillary tube was connected by means of rubber tubing to a capillary tube with two stop-cocks so arranged that passage between the vapourizing vessel and the burette could be cut off, and so that the pressure in the former could be kept at atmospheric pressure. The other end of the tubing was connected to the burette by means of rubber tubing. The breaking apparatus consisted of a piece of glass tubing 24 cm. long in which was placed a brass rod 27 cm. long. One end of the rod was filed so as to form a hook in which the capillary of the containing bulb was held. The rod was held in the tube by means of a piece of rubber tubing. To break the bulb the rod was pulled up, thereby breaking the capillary of the bulb by pressure against the glass tubing, the bulb being suspended as shown in the vapourizing vessel. The burette was calibrated from a hairline at the top and all volumes were corrected by means of a graph plotted from figures obtained in the calibration. The temperature of the water bath surrounding the burette was observed.

In making a determination the bulb with the weighed substance was suspended on the breaking apparatus and placed in the vapourizing vessel, the rubber stopper being placed

firmly in the neck of the apparatus. Both stop-cocks were opened, and the level of the water in the burette brought to the hair-line at the top. Heating was continued for I5 minutes as this was found by experiment to be the minimum time permissible for heating all parts to the temperature of the vapour. When heating was completed, the stop-cock opening to the atmosphere was closed, the leveling bulb on the burette was lowered to create a partial vacuum, and the bulb was broken by raising the brass rod. Vapourization was usually very rapid, depending upon the boiling point of the substance used for the bath and the substance whose molecular was being determined. The air was brought to atmospheric pressure by means of the leveling bulb, and the stop-cock controlling the burette immediately closed. The air was then allowed to stand for at least I5 minutes in the burette so as to be sure to have it at the same temperature as the surroundig water bath. While the air was cooling, the breaking apparatus was removed, the stop-cock on the side-tube opened, and the vapour in the vapourizing vessel removed by inserting a tube connected with a vacuum. Another bulb was then placed on the breaking apparatus and inserted in the vapourizing vessel and heated to the temperature of the vapour bath while the air displaced in the previous run was cooling to the temperature of the water bath.

Determinations were made with bromine, ethyl ether, and benzene, using a water bath in most cases. A linseed oil bath was also used with bromine and benzene and it was found that difference in temperature the vapour and the the boiling point of the substance must be at least 30°. Some of the

results obtained are given in table No.I. These are selected.

TABLE No. I.

BROMINE[a]

Weight of Substance	.1369	.1572	.1466	.1553
Corrected Volume	20.94	24.33	22.84	24.16
Temperature	24.1	24.1	25	25
Relative Humidity	38	38	46	46
Atmospheric Press.	74.986	74.986	73.891	73.891
Vapor Pressure	2.23	2.23	2.35	2.35
M.W. by Gas Law	164.[illegible]	162.58	164.31	164.52
M.W. by Berthelot	160.[illegible]	158.8	160.5	160.7
M.W. accepted	159.5	----	----	----

[a]T_c, 375°; P_c, 86.4

ALCOHOL[b]

Weight of Substance	.0476	.0592	.0499	.0459
Corrected Volume	26.01	31.79	27.04	25.01
Temperature	26.2	25	25	25.5
Relative Humidity	47	51	51	47
Atmospheric Press.	74.698	74.612	74.612	74.598
Vapor Pressure	2.53	2.35	2.35	2.42
M.W. by Gas Law	46.58	47.12	46.69	46.61
M.W. by Berthelot	46.11	46.66	46.22	46.14
M.W. accepted	46.05	----	----	----

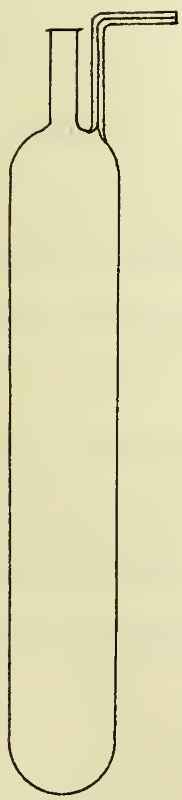
[b]T_c, 509°; P_c, 64

CARBON DISULPHIDE[e]

Weight of Substance	.0837	.1199	.0963	.0798
Corrected Volume	27.87	40.84	32.68	28.31
Temperature	27.5	29	29	29
Relative Humidity	43	39	39	39
Atmospheric Press.	74.80	74.80	74.80	74.80
Vapor Pressure	2.73	2.98	2.98	2.98
M.W. by Gas Law	77.05	75.81	76.07	76.41
M.W. by Berthelot	76.95	75.86	75.96	76.25
M.W. accepted	76.14	----	----	----

[e]T_c, 547°; P_c, 75

It was found that results were not consistent, and tests were made to determine whether or not the vapour of the substance experimented with had passed over into the burette. Potassium iodide starch paper was placed in the end of the capillary tube when bromine was being used, and it was found that the bromine vapour passed over with nearly every determination as was shown by the coloring of the starch paper. It was decided that the tube passing around the vessel was unnecessary, and that the capacity was too small. It was also a very fragile piece of apparatus, great care being required in manipulation.



The next type of vapourizing vessel experimented with was that shown in figure IV. Its advantages over the first apparatus were that it had a much larger capacity and yet could be used in the same heating vessel, and it was much less fragile. The diameter of the cylinder was 5 cm., and the length 22 cm., giving it a volume almost three times as great as the first apparatus. Results were fairly consistent, but sometimes vapor was found to have passed over into the burette. The greatest trouble seemed to be in directing the vapour from the bulb downward, and thereby prevent its reaching the capillary tube before it had displaced an equivalent amount of air. As an improvement in

this detail, the containing bulb shown in figure V. was devised. It consisted of a tube 3 mm. in diameter and 2 cm. long, closed at one end and the other end drawn into a capillary and bent as shown. This was placed in the hook on the breaking apparatus and fastened to the latter with a rubber band, so that upon breaking the vapour would be directed downward. Glass beads were placed in the bottom of the vapourizing vessel to break the force of the stream of vapour and thus decrease its tendency to diffuse quickly and pass into the burette. No appreciable improvements were found in the results, but the bulbs were much easier to make, and it was easier to judge the amount of substance in the bulbs as they were all of the same diameter, while it was difficult to make bulbs of the first type uniform in size.

Firure V.

Although this apparatus was not as fragile as that first used, great care had to be taken to avoid breaking the outside tube, as it broke easily at the connection with the cylinder. In order to be sure that no vapour passed over into the burette it was necessary to use smaller amounts of substance than was desirable. Some results obtained with this apparatus are given in table No. II. These are selected.

TABLE No. II.

BROMINE[a]

Weight of Substance	.I637	.I773	.I594	.I69[illegible]
Corrected Volume	25.I4	27.33	24.96	26.67
Temperature	25.5	25.5	26.2	26.2
Relative Humidity	43	43	44	44
Atmospheric Press.	74.9I7	74.9I7	73.86I	73.86I
Vapor Pressure	2.42	2.42	2.55	2.55
M.W. by Berthelot	I6I.I	I60.5	I6I.3	I59.9
M.W. accepted	I59.8	----	----	----
M.W. by Gas Law	I64.9	I64.3	I65.I	I63.6

[a]T_c, 375°; P_c, 86.4

BENZENE[b]

Weight of Substance	.I255	.II48	.II60	.I359
Corrected Volume	38.84	35.90	35.98	42.87
Temperature	23	23.5	23	25.5
Relative Humidity	5I	6I	52	58
Vapor Pressure	2.08	2.03	2.08	2.43
Atmospheric Press.	74.43	74.37	74.37	74.82
M.W. by Gas Law	79.99	80.I3	8I.I2	80.00
M.W. by Berthelot	78.39	78.53	79.48	78.40
M.W. accepted	78.04	----	----	----

[b]T_c, 559.4°; P_c, 49.2

ALCOHOL[e]

Weight of Substance	.0799	.0537	.0487	.05I0
Corrected Volume	43.42	29.06	26.28	27.64
Temperature	25	24.5	24.5	23.5
Relative Humidity	48	48	48	47
Vapor Pressure	2.35	2.29	2.23	2.I5
Atmospheric Press.	73.687	73.965	73.965	73.595
M.W. by Gas Law	47.02	47.I0	47.24	46.9I
M.W. by Berthelot	46.50	46.63	46.77	46.44
M.W. accepted	46.05	----	----	----

[e]T_c, 509.°; P_c, 64

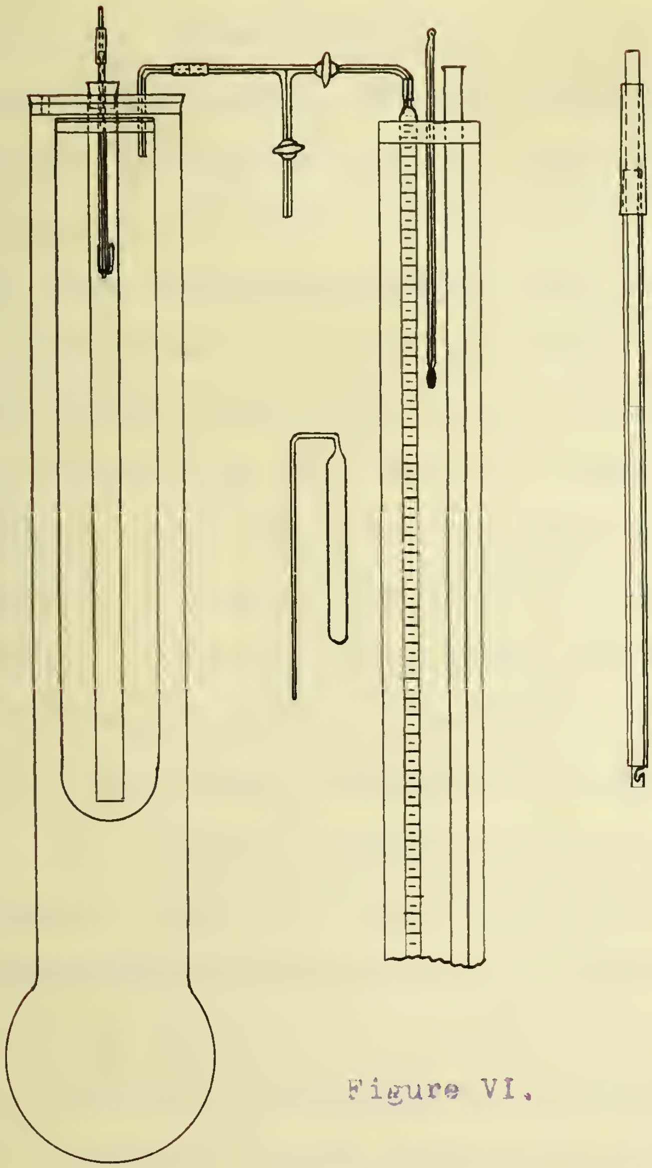


Figure VI.

With the idea in view of correcting the faults of the apparatus previously used, the apparatus shown in figure VI. was constructed. It consisted of a cylinder 5 cm. in diameter and 24 cm. long, closed at one end and open at the other. This was fitted with a two hole rubber stopper, one hole in the center thru which a tube 1.5 cm. in diameter and 25 cm.

long was admitted,and the other near the edge to admit a 1 mm. capillary tube which served as an outlet for the air in passing to the burette. The outer jacket was provided with a three hole rubber stopper,the third hole being for a steam outlet. The breaking apparatus and bulbs used were the same as those used previously,only that the former was but 10 cm. long,so that the bulb was held near the top of the inner tube. This apparatus was used with the same burette,and tests were made to see if any vapour passed over,but in no case did the test paper show any coloration before the stop-cock controlling the burette had been closed. In order to reach the capillary exit the vapour had to pass down to the bottom of the inner tube,which was about 1 cm. above the bottom of the vapourizing vessel,and then pass to the top of the latter,but in all cases,before it had diffused that far,it had already displaced an equivalent amount of air.

The complete operation in making a determination may be summarized as follows. The apparatus is set up as in the diagram,and the substance in the outer jacket heated. The stop-cock opening to the outside must be opened to avoid breaking of the apparatus by the expansion of the air in the vapourizing vessel,because if this precaution is not observed the pressure created will force out the stopper, thereby causing considerable work to set it up again,and possibly breaking either the vapourizing vessel or the outer jacket by the impact of the two. An asbestos board was placed between the outer jacket and the burette to prevent the latter from being heated by the flame under the outer jacket. It was found that a sand bath served to keep

the boiling more constant than a free flame. While heating, bulbs may be made from a 3 mm. glass tube by drawing it out into capillaries at intervals of every 2 cm. and cutting the capillaries near the end of a tube. The end of the tube is then sealed, and the capillary end bent in the desired shape and cut to the proper length. The bulbs are then weighed. They are then filled by heating in a flame, and immersing the capillary in the substance to be used, the latter being in a I inch test tube. Upon cooling, the air in the bulb contracts and the substance is forced in, When the desired amount has been taken in, the bulb is removed, and the capillary is sealed by means of a blow-pipe and flame. If in filling the bulb, too much substance has been taken in, the excess may be removed before sealing by slightly heating the bulb. The bulb and substance are then weighed, the difference in the two weights being the weight of the substance taken. The breaking apparatus is then removed and the capillary of the bulb placed in the hook of the former. The bulb is not suspended, but is inverted and fastened onto the breaking apparatus with a small rubber band. The breaking apparatus is then placed in the inner tube and the rubber stopper placed firmly in the former. Heating is continued for a minimum of I5 minutes, and in the meantime, if it has not already been done, the stop-cock leading to the burette is opened and by means of the leveling bulb the water in the burette is brought to the zero line. When heating is completed the stop-cock opening to the outside is closed, the leveling bulb lowered to create a partial vacuum, and the capillary of the bulb broken by raising the brass rod. In raising this rod, care must be

taken that the stopper is not removed, for some times consid-erable force is required to break the capillary. The displaced air in the burette is quickly brought to atmospheric pressure with the leveling bulb, and the stop-cock leading to the for-mer is closed.. The displaced air must stand for at least 15 minutes before its volume is taken. The stop-cock opening to the outside is then opened, the breaking apparatus removed, and the vapour in the vessel removed by inserting a tube connected with a vacuum. When the vapour has been completely removed, another bulb may be put in and the complete opera-tion repeated.

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This apparatus is very easily constructed and gives good, consistent results. Some of the results obtained are given in table No. III. These are not selected; the first four and the last three sets of data in each table having been obtained at the same time. They are very representative of the consistency of all results obtained.

TABLE No. III.

BROMINE[a]

Weight-Substance	.1970	.2015	.1475	.2059	.1861	.1699	.1809
Corrected Volume	30.33	31.05	22.71	31.05	29.00	26.42	25.31
Temperature	24	25	23	25	24.5	24.5	24.5
Relative Humidity	49	47	49	47	48	48	48
Vapor Pressure	2.22	2.35	2.08	2.35	2.28	2.28	2.28
Atmospheric Press.	74.645	74.645	74.645	74.645	73.965	73.965	73.965
M.W. by Gas Law	163.70	164.40	163.01	166.86	163.81	164.03	162.95
M.W. by Berthelot	159.9	160.6	159.5	163.0	160.04	160.25	159.26
M.W.- accepted	159.8	----	----	----	----	----	----

[a]T_c, 375°; P_c, 86.4

ALCOHOL[b]

Weight-Substance	.0494	.0612	.0561	.0587	.0599	.0486	.0527
Corrected Volume	27.23	33.68	30.54	32.04	33.51	26.53	28.58
Temperature	23.5	23.5	23.5	23.5	25	25	25
Relative Humidity	47	47	47	47	51	51	51
Vapor Pressure	2.15	2.15	2.15	2.15	2.35	2.35	2.35
Atmospheric Press.	73.617	73.617	73.617	73.617	74.612	74.612	74.612
M.W. by Gas Law	46.31	46.83	46.89	46.72	46.51	46.37	46.69
M.W. by Berthelot	45.85	46.36	46.42	46.25	46.14	45.91	46.22
M.W. - accepted	46.05	----	----	----	----	----	----

[b]T_c, 509°; P_c, 64

TABLE No.III.

ETHER[a]

Weight-Substance	.0866	.0637	.08II	.073I	.0937	.0957	.1040
Corrected Volume	29.46	2I.84	27.54	24.91	31.97	32.84	35.90
Temperature	25	25	25	25	29	30	3I
Relative Humidity	5I	5I	5I	5I	59	59	60
Vapor Pressure	2.35	2.35	2.35	2.35	2.97	3.15	3.34
Atmospheric Press.	73.287	73.287	73.287	73.287	73.865	73.865	73.865
M.W. by Gas Law	75.76	75.I6	75.9I	75.64	76.02	75.9I	75.69
M.W. by Berthelot	74.24	73.66	74.39	74.12	74.50	74.38	74.I8
M.W. - accepted	74.08	----	----	----	----	----	----

[a] T_c, 467.I; P_c, 36.2

IV. CONCLUSION

Several new types of apparatus for the determination of vapor densities by the Victor Meyer method have been experimented with, and each one will, with the proper precautions, give better results than the original apparatus. The last piece of apparatus used is the one most easily constructed, and it was found to give the most consistent results.